

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
16 October 2003 (16.10.2003)

PCT

(10) International Publication Number
WO 03/084644 A1

(51) International Patent Classification⁷: **B01D 53/04**

(21) International Application Number: PCT/IB03/01247

(22) International Filing Date: 7 April 2003 (07.04.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI2002A000715 5 April 2002 (05.04.2002) IT

(71) Applicant (for all designated States except US): **PO-LARIS S.R.L.** [IT/TT]; Via Zucchi, 1, I-20052 Monza (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MASETTO, Gian, Claudio** [IT/TT]; MASETTO, Gian, Claudio, Via D'Azeglio, 2, I-20052 Monza (IT). **MASETTO, Mario** [IT/TT]; Via Grossi, 6, I-20052 Monza (IT). **MASETTO, Francesco** [IT/TT]; Via Tazzoli, 37, I-20052 Monza (IT).

(74) Agent: **PREMRU, Rok**; Via De Amicis, 4, I-20052 Monza (IT).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

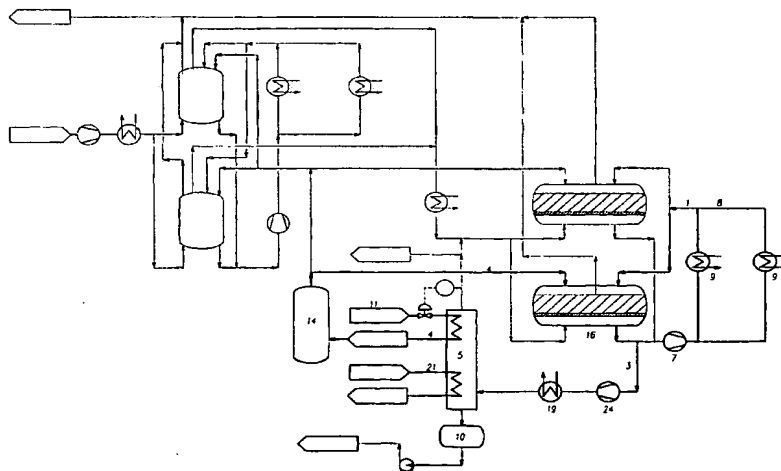
— of inventorship (Rule 4.17(iv)) for US only

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD AND SYSTEM FOR DESORPTION AND RECOVERY OF DESORBED COMPOUNDS



(57) Abstract: A method for desorption and recovery of desorbed compounds, including the steps of generating a recirculating stream of inert gas (1), which passes through the material (2) to be desorbed, heating such inert gas stream to a temperature sufficient to cause the desorption process, yielding a gas effluent (3) from such recirculating stream of inert gas (1) in such a manner that the recirculated gas keeps a constant pressure, cooling such gas effluent to cause condensation of the desorbed compounds contained in such gas effluent (3), said cooling being obtained at least partly by pressure vaporization of a cryogenic fluid (4), and feeding such recirculating gas stream (1) by using at least a part of such pressure vaporized cryogenic fluid that was previously used to cool at least a part of the gas effluent (3).

WO 03/084644 A1

METHOD AND SYSTEM FOR DESORPTION AND RECOVERY OF
DESORBED COMPOUNDS

TECHNICAL FIELD

This invention relates to a method and a system for desorption and recovery of desorbed compounds.

BACKGROUND ART

It is a common practice to use the adsorption technique, on adsorbent beds of materials like activated carbons, macroporous resins, molecular sieves, zeolites and activated alumina, to separate volatile organic compounds (VOCs), as well volatile inorganic compounds, which are present as pollutants in gas emissions of industrial processes and, for process reasons, in liquid or gas mixtures which are formed in many industrial production processes.

It is also known to regenerate adsorbent materials to allow reuse thereof in several cycles, by means of desorption and recovery of the volatile compounds released from the adsorbent material, for reuse or disposal thereof.

For such purpose, adsorbent materials must be heated by convection (using steam or other fluids), or by conduction (indirect heat exchange), or by radiation (for example, using microwaves), to supply the adsorbed compounds with the energy needed for desorption thereof.

Although the use of steam is effective, it often causes partial hydrolysis of the compounds to be desorbed, and serious corrosion problems, and at all

events the formation of huge amounts of condensed water mixtures to be processed to allow reuse or disposal thereof.

Indirect heat exchange, although associated with vacuum, requires unacceptable operation times for industrial applications, as adsorbent materials typically have a poor heat transfer coefficient.

US-A-5,779,768 (ANAND) discloses regeneration of adsorbent materials by using a stream of hot inert gas, e.g. nitrogen, which passes through the material to be regenerated.

The gas stream provides a sufficient amount of heat energy for the adsorbed compounds to break their bonds with the adsorbent materials, and the hot stream strips the compounds released from the adsorbents, in form of vapors.

In steady conditions, the gas enriched in desorbed compounds is delivered, totally or partially, to a condenser where it is cooled to a temperature below the dew point, to obtain condensation of the adsorbed compounds (except a small portion that remains in the vapor phase), for reuse or disposal thereof.

According to this prior art technique, throughout the process, the whole gas stream must be simultaneously heated (upstream from the bed of material to be regenerated) and cooled (downstream from the bed); this also occurs in other prior art techniques.

When considering the high flow rates (usually at least twice the adsorption flow rates) that are needed

to carry out regeneration in short times, the high temperatures required for regeneration of the adsorbent material and, conversely, the low cooling temperatures that are needed to condensate the separated volatile compounds, it is apparent that this prior art technique requires the simultaneous supply of huge heating and cooling powers to the gas stream used for desorption and recovery of volatile compounds.

Therefore, this prior art technique requires complex and expensive systems, particularly requiring high running costs, whose increase is inversely proportional to the cooling temperature required to obtain a good regeneration of the adsorbent material.

Also, it might produce an unsatisfactory level of adsorbent material regeneration, when compared with the increasingly strict emission limits prescribed in many countries for environment protection.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method and a system which might at least partly obviate the drawbacks of prior art techniques, and particularly reduce power consumption and improve the level of regeneration of adsorbent materials.

This object is achieved by a method according to the wording of claim 1 and by a system according to the wording of claim 6.

Further advantages may be obtained by the additional features described in the dependent claims 2 to 5 and in the dependent claim 7.

BRIEF DESCRIPTION OF THE DRAWINGS

A possible embodiment of method and system, according to the wording of the patent claims, will be described hereafter, with reference to the attached drawings, in which:

- Fig.1 is a flow diagram of a system designed for desorption and recovery of desorbed compounds according to a first embodiment;

- Fig. 2 is a flow diagram of a system designed for desorption and recovery of desorbed compounds according to a further embodiment.

DISCLOSURE OF THE INVENTION

With reference to the figures of this patent, the method for desorption and recovery of desorbed compounds includes the steps of generating a recirculating stream of inert gas 1, which passes through the material 2 to be desorbed, and heating such inert gas stream to a temperature sufficient to cause the desorption process.

The method further includes the steps of yielding a gas effluent 3 from the recirculating stream of inert gas 1, in such a manner that the recirculated gas 1 keeps a constant pressure, which would otherwise tend to increase because of both the rise of temperature and the release of volatile compounds following the desorption process, and delivering the gas effluent 3 to means 5 and 6, fit for cooling the gas effluent 3 and causing condensation of the desorbed compounds contained therein.

In steady conditions, the temperature of the recirculating gas stream 1 may be of 370 to 470 °K,

whereas the temperature of the gas effluent 3 inside the means 5 or 6 may be as low as 100 to 130 °K, to obtain condensation of desorbed compounds.

The heating temperature depends on the nature of the adsorbent material to be regenerated, whereas the cooling temperature depends on the nature of the desorbed compounds to be recovered.

The means 5 and 6 for obtaining condensation of desorbed compounds may consist of a cryogenic condenser 5 or an internal reflux fractionation column 6, as the one described in detail in EP-B1-0513704, which is hereby incorporated by reference.

The cooling capacity of the above means 5 or 6 required for condensation of desorbed compounds is obtained, at least partly, by vaporization of a cryogenic fluid 4, i.e. by using a liquefied gas.

Inside the condenser 5, or fractionation column 6, the cryogenic fluid 4 evaporates under pressure, thereby absorbing heat from the gas effluent 3 coming from the recirculated stream 1.

The gas effluent 3, fully purified after the separation of volatile compounds, can be vented to the atmosphere, while the condensed desorbed compounds are recovered for further reuse or disposal.

The evaporated cryogenic fluid 4 used by the means 5 or 6 to cool the gas effluent 3 is further delivered, at least partly, to the recirculating stream 1, to allow clean gas addition to such stream 1.

In the preferred embodiment, the cryogenic fluid 4 is liquid nitrogen, which is particularly suitable

because its dew point is lower than that of the compounds to be recovered, because it is easily available at a low price, and because it is inert and harmless for the environment.

In a preferred embodiment, pressurized nitrogen 4 is introduced in the recirculated stream 1 with the help of a storage tank 14.

By way of indication, the average flow rate of the nitrogen 4 introduced in the recirculated stream 1 may be about 1% of the flow rate of the recirculated stream 1.

The evaporated nitrogen 4 continuously introduced in the recirculating stream, as well as the continuously released desorbed volatile compounds, are continuously compensated for by the effluent 3, whereby the recirculated gas pressure 1 remains substantially constant with time.

Preferably, the average flow rate of the gas effluent 3 is below 1/50 of that of the recirculated stream 1, and more preferably the flow rate of the gas effluent 3 is below 1/100 of the flow rate of the recirculated gas stream.

Those skilled in the art will appreciate that this solution allows to operate at low cooling powers, thanks to the fact that not the whole gas stream passing through the material to be regenerated shall be cooled, but only a small part thereof (typically 1 to 2% of the hot gas stream that passes through the material to be regenerated).

Due to the possibility of using low cooling

powers, it is technically and commercially advantageous to use liquefied gas as a coolant; this allows to operate at very low temperatures, and to obtain an effective removal of the desorbed compounds contained in the gas effluent 3.

Those skilled in the art will also appreciate that this solution allows to operate, in steady conditions, with very low heating powers, thanks to the fact that the recirculated stream 1 is not simultaneously cooled; by simply heating the clean gas 4, introduced into the stream closed loop, the gas effluent 3 may be compensated for and the heat energy released to the adsorbent material and to the system may be reintegrated.

Yet, those skilled in the art will appreciate that the continuous introduction of clean gas into the recirculating stream 1 allows a better regeneration of the adsorbent material 2, due to the reduced concentration of desorbed compounds, which provides a favourable condition for desorption.

In order to obtain full regeneration of the material 2, the desorption process preferably includes the additional steps of stopping the delivery of the evaporated cryogenic fluid 4, stopping the circulation of the recirculating gas stream 1 and sucking in the recirculated gas 1 until a negative pressure is generated inside the bed of the adsorbent material to be regenerated 2, in such a manner as to create new favorable thermodynamic conditions for desorption.

The required energy is provided by the heat

capacity of the (adsorbent and adsorbed) materials, which are cooled thereby.

All the above steps may be repeated several times, to obtain a more effective regeneration of the adsorbent material.

The above method may be implemented by using a system for desorption and recovery of desorbed compounds, which comprises a closed loop 8, with a vessel 16, containing a bed of adsorbent material 2, and means 7 for generating a recirculating stream of inert gas 1 in the closed loop 8.

Typically, the means 7 for generating a recirculating stream of inert gas 1 include a fan 7, which keeps the flow rate and the pressure of the recirculating stream 1 at a substantially constant level with time.

Means 9 are further provided for heating the recirculated gas stream 1 in the closed loop 8, which means 9 may typically include a steam heat exchanger, or hot oil heat exchanger or a resistive heat exchanger.

A duct 10 branches off the closed loop 8 to allow discharge of the effluent 3, caused by gas pressure and volume increases in the loop 8, so as to keep the average internal pressure value of the recirculating gas in the loop 8 substantially constant with time.

A cryogenic condenser 5, or an internal reflux fractionation column 6 is provided to receive the effluent 3 from the duct 10.

In the embodiment as shown in Fig. 1, the

cryogenic condenser 5 is fed, in its lower portion, with a coolant 21 (such as cold water) and, in its higher portion, with liquid nitrogen coming from a tank 11.

Preferably, the gas effluent 3 is pre-cooled, before being introduced into the cryogenic condenser 5, by using coolants 19.

An inexpensive coolant for the cooling means 19 may be cooling tower water.

After the purification, the gas effluent 3 may be released to the atmosphere, whereas the condensed desorbed compounds are collected in a special tank 10, possibly cooled if gas is in the liquid phase.

The cryogenic condenser 5 is cooled by using liquid nitrogen 4, delivered from a tank 11, and evaporating under pressure in the condenser 5.

The nitrogen outflow from the condenser 5 or the fractionation column 6 is delivered under pressure to a storage tank 14 and from the latter to the closed loop 8.

The desorption system further includes special cutoff means 13, which are designed to stop the evaporated cryogenic fluid supply 4 to the closed loop 8, means 24 for sucking in the gas contained in the closed loop 8 to generate a pressure below atmospheric pressure in the container 6.

Preferably, the means 14 consist of a vacuum pump which may decrease the pressure inside the container to values of about 2 to 5 mBar.

Those skilled in the art will appreciate that the

method may favor the use of macroporous resins in volatile and liquid organic and inorganic compound adsorption processes.

These resins are not widely used in prior art, due to their thermal lability, which prevents regeneration thereof at high temperatures, which drawback is obviated thanks to the new technique, by implementing a heating protocol at relatively low temperatures and a desorption protocol at high vacuum degrees, and by using an inert heating medium that does not interact chemically with the adsorbent material.

The advantages of these resins are their low adsorption and desorption power requirements, the absence of active catalysis sites, the latter being present in activated carbons, and consequent benefits in terms of lower management costs and a higher operational safety.

Furthermore, the new technique provides full removal of volatile impurities captured by the resins during manufacture, which might prevent them from being used in the medical and biotechnological fields.

Finally, those skilled in the art will appreciate that the use of an internal reflux fractionation column 6 for cryogenic condensation, as shown in Fig. 2 provides a simultaneous fractionation of the desorbed compounds supplied thereto, even when the latter are composed of gas mixtures.

Fractioning may be completed in the same column, thereby providing further savings on investment and management costs.

In the embodiments of Figures 1 and 2, the desorption system can alternately operate on two vessels 16.

Hence, one of the two vessels 16 is always ready for adsorption of the gas emissions to be cleaned.

EXAMPLE 1

By using the system design of Fig. 1, corresponding to the preferred embodiment of this invention, the following results were obtained for a representative case of removal and recovery of volatile organic compounds, by only using liquid nitrogen in the cryogenic condenser:

<u>Stream inlet conditions</u>		<u>Stream outlet conditions</u>	
Temperature	40 °C	Temperature	35 °C
Pressure	AP	Pressure	AP
Flow rate	9,535 kg/h	Flow rate	9,122 kg/h
<u>Composition w/w</u>		<u>Composition</u>	
Acetone	0.42 %	Acetone	9 mg/m ³
Methylene chloride	1.15"	Methylene chloride	10"
Isopropyl alcohol	0.33"	Isopropyl alcohol	16"
Moisture	1.91"	Moisture	None
Air	95.66"	Air remaining percentage	

Outlet conditions of the stream from the cryogenic condenser

Temperature -130 °C

Pressure AP

(Average) flow rate 160 kg/h

Composition

Acetone 1 mg/m³

Methylene Chloride 2 mg/m³

Isopropyl alcohol undetectable

Moisture None

Oxygen (blowdown) 20 % to 1 %

Oxygen (regen.) traces

Nitrogen remaining percentage

Solvent recovery yield 99.85 % (724.3 out of 725.4 introduced per cycle)

The above performances may be obtained with the following system:

Bed of activated carbon 6000 kg

Adsorption cycle 4 hours

Desorption cycle 4 hours

Adsorption temperature 30 °C

Desorption temperature 160 °C

Flow rate in the desorption loop 20000 m³/h

Temp. at the inlet of the cryogenic condenser 50 °C

Absolute min. press. upon desorption 0.5 mbar

Pressure of the recovered nitrogen 6 barG

Power consumption per cycle 280 kWh

Nitrogen consumption per cycle 640 kg

Steam consumption per cycle 830 kg

Cooling water (cycle) 30 m³

Pre-cooling water (cycle) 720000 kcal

EXAMPLE 2

By using the system design as shown in Fig. 2, corresponding to a second preferred embodiment of this invention, an internal reflux column being integrated therein, the following results were obtained for a representative case of removal and recovery of volatile organic compounds simultaneous with fractionation thereof, by only using liquid nitrogen and cooled glycol in the cryogenic internal reflux column:

Stream inlet conditions Stream outlet conditions

Temperature 50 °C	Temperature 35 °C
Pressure AP	Pressure AP
Flow rate 880 kg/h	Flow rate about 880 kg/h
<u>Composition w/w</u>	<u>Composition</u>
Freon 11 1.29 %	Freon 11 6 mg/m ³
n-Pentane 0.41	n-Pentane 2 mg/m ³
Moisture 1.63	Moisture None
Air remaining percent.	Air remaining percent.

Outlet conditions of the stream from the cryogenic internal reflux column after final condensation

Temperature -150 °C
Pressure AP
(Average) flow rate 40 kg/h
Composition
Freon 11 2 mg/m³
n-Pentane none

Moisture None

Oxygen (blowdown) 20 % to 1 %

Oxygen (regen.) traces

Remaining nitrogen

Solvent recovery yield 99.96% (59.82 out of 59.84 introduced per cycle)

Recovered Freon (cycle) 45.4 kg

Recovered n-Pentane (cycle) 14.4 kg

The above performances were obtained by using the following system:

Bed of activated carbons 600 kg

Absorption cycle 4 hours

Desorption cycle 4 hours

Adsorption temperature 35 °C

Desorption temperature 160 °C

Flow rate in the desorption loop 1600 m³/h

Temp. at the inlet of the cryogenic condenser 50 °C

Min. press. upon desorption 0.5 mbar

Pressure of the recovered nitrogen 6 barG

Power consumption per cycle 54 kWh

Nitrogen consumption per cycle 210 kg

Steam consumption per cycle 120 kg

Cooled water for regeneration 4 m³

Cooled water for the column 90000 kcal

The above power consumptions include those used for fractioning the Freon 11 and the n-Pentane.

CLAIMS

1. A method for desorption and recovery of desorbed compounds, including the steps of:

- generating a recirculation stream of inert gas (1) which passes through the material (2) to be desorbed;

- heating said stream (1) to a temperature sufficient to cause the desorption process;

- yielding a gas effluent (3) from said recirculating stream of inert gas (1) in such a manner that said recirculated gas (1) keeps a constant pressure

- cooling said gas effluent (3) to cause condensation of the desorbed compounds contained in said gas effluent (3), said cooling being obtained at least partly by pressure vaporization of a cryogenic fluid (4);

- feeding said recirculating gas stream (1) by using at least a part of said pressure vaporized cryogenic fluid (4) that was previously used to cool at least a part of said gas effluent (3).

2. A method for desorption and recovery of desorbed compounds as claimed in claim 1, wherein the flow rate of said gas effluent (3) outflown from said recirculating gas flow (1) is below 1/50 of the flow rate of the recirculated stream (1).

3. Method for desorption and recovery of desorbed compounds as claimed in claim 1 or 2, wherein said cooling of said gas effluent (3) is obtained by means of a cryogenic condenser (5).

4. Method for desorption and recovery of desorbed compounds as claimed in claim 1 or 2 or 3, wherein said cooling of said gas effluent (3) is obtained by means of an internal reflux fractionation column (6).

5. A method for desorption and recovery of desorbed compound as claimed in any preceding claim, including the additional steps of:

- stopping the delivery of said evaporated cryogenic fluid (4), which is used to cool at least a part of the gas effluent (3), to the recirculating stream (1);

- stopping the circulation of said recirculating stream of inert gas (1);

- sucking in the recirculated gas (1) to generate a negative pressure in the bed of material to be regenerated (2), and delivering the sucked gas to said desorbed compound condensing means (5; 6).

6. A system for desorption and recovery of desorbed compounds, including:

- a vessel (16) containing a bed of adsorbent material (2);

- means (17) for generating a recirculating stream of inert gas (1) in a closed loop (8) which includes said vessel (6);

- means (9) for heating said recirculating gas stream (1) in said closed loop (8);

- a cryogenic condenser or an internal reflux fractionation column (6), which is at least partly cooled by an evaporated cryogenic fluid (4);

- a duct (10) for connecting said closed loop (8)

to said cryogenic condenser (5) or said internal reflux fractionation column (6), to feed a gas effluent (3) coming from said closed loop (8) to said cryogenic condenser (5) or said internal reflux fractionation column (6);

- means (12) for delivering a part of said evaporated cryogenic fluid (4) outflow from said condenser (5) or said fractionation column (6) to said closed loop (8).

7. A system as claimed in claim 6, which further includes:

- means (13) for stopping the feed of evaporated cryogenic fluid to said closed loop (8);

- means (14) for sucking in the gas in said closed loop (8) to generate a pressure below atmospheric in said vessel (16).

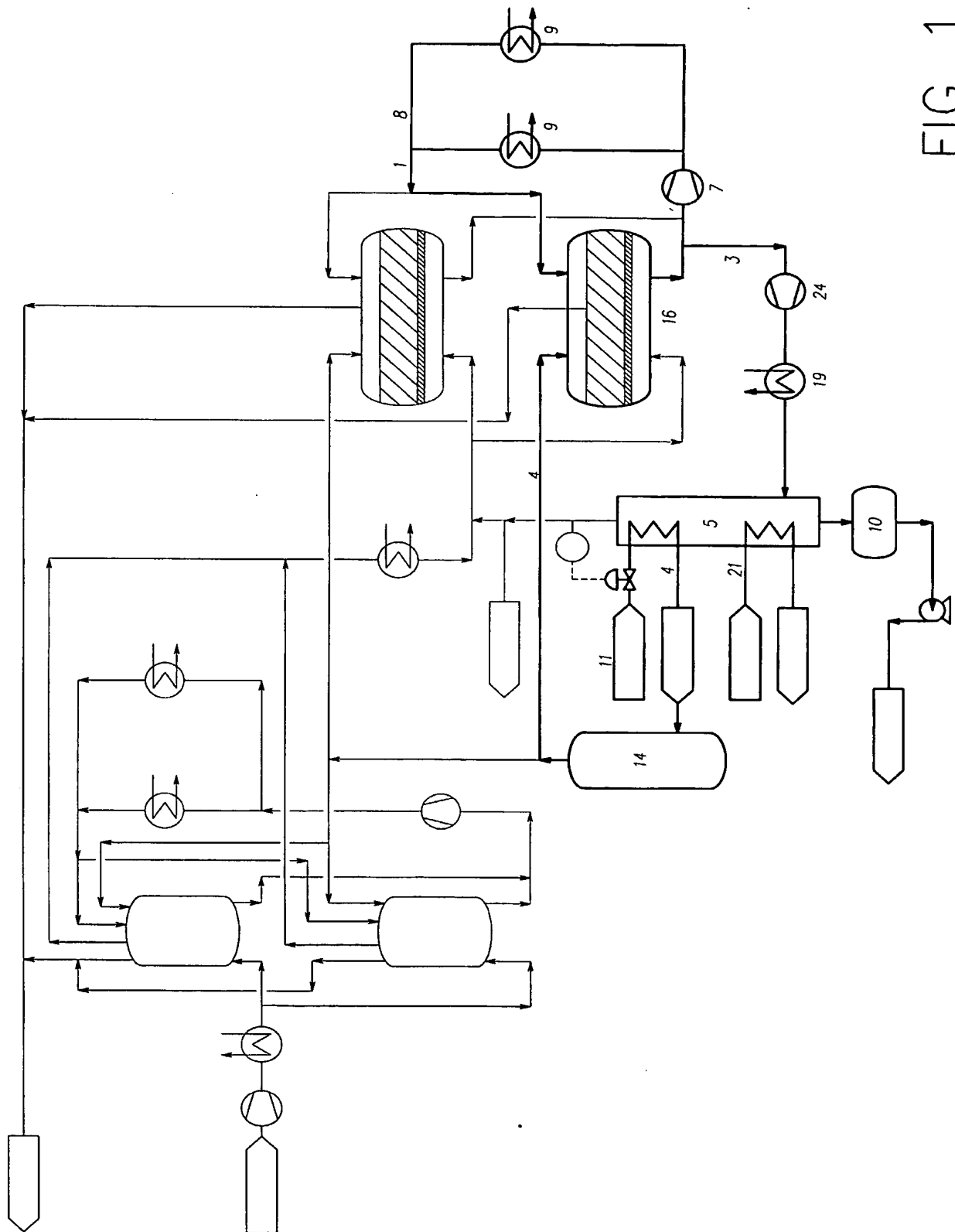


FIG. 1

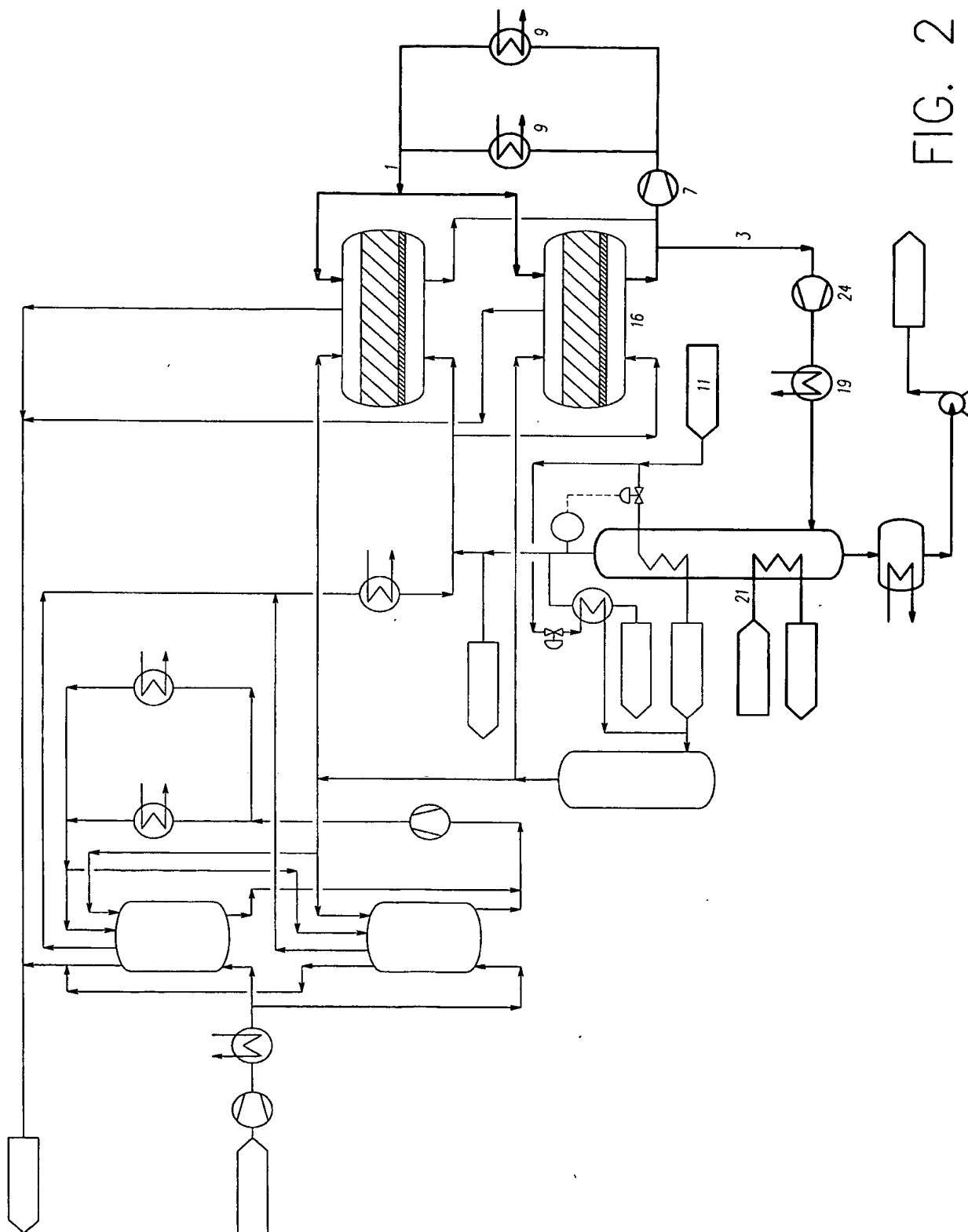


FIG. 2

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/IB 03/01247

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 421 532 A (SACCHETTI MASSIMO ET AL) 20 December 1983 (1983-12-20) claim 1; figure 1 ---	1,6
A	US 4 480 393 A (FLINK LESLIE R ET AL) 6 November 1984 (1984-11-06) column 5, line 1 - line 6; claims 1-3; figure 2 ---	1,6
A	US 5 779 768 A (ANAND MADHU ET AL) 14 July 1998 (1998-07-14) cited in the application column 3, line 50 -column 528; figure 1 ---	1,6
A	DE 195 03 052 A (BRESCH ENTSORGUNG GMBH) 8 August 1996 (1996-08-08) column 2, line 1-42; claims 1,2; figure 1 --- -/--	1,6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

10 June 2003

Date of mailing of the international search report

20/06/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

de Blasio, A

INTERNATIONAL SEARCH REPORT

Internatⁿ Application No
PCT/IB 03/01247

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 043 770 A (JAKOB FRITZ) 23 August 1977 (1977-08-23) column 4, line 1 - line 33; figures 1,2 -----</p>	1,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 03/01247

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4421532	A	20-12-1983	IT 1062296 B 26-06-1984
		AT 4780 T 15-10-1983	
		CA 1176183 A1 16-10-1984	
		DE 3161028 D1 03-11-1983	
		EP 0046141 A1 17-02-1982	
		ES 8205361 A1 01-10-1982	
US 4480393	A	06-11-1984	AU 552970 B2 26-06-1986
		AU 8584582 A 04-01-1983	
		BR 8207748 A 10-05-1983	
		DE 3280108 D1 15-03-1990	
		EP 0081558 A1 22-06-1983	
		JP 58500938 T 09-06-1983	
		WO 8204475 A1 23-12-1982	
US 5779768	A	14-07-1998	NONE
DE 19503052	A	08-08-1996	DE 19503052 A1 08-08-1996
		AU 4384696 A 21-08-1996	
		CA 2186884 A1 08-08-1996	
		WO 9623574 A1 08-08-1996	
		EP 0755297 A1 29-01-1997	
		ZA 9600487 A 15-07-1996	
US 4043770	A	23-08-1977	DE 2460515 A1 01-07-1976